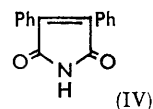
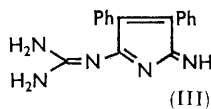
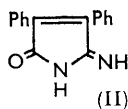
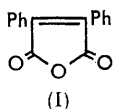


409. *The cis- and trans- $\alpha\beta$ -Dicyanostilbenes. Part II.*<sup>1</sup>  
*Authentic cis- $\alpha\beta$ -Dicyanostilbene.*

By M. V. SARGENT and C. J. TIMMONS.

*cis- $\alpha\beta$ -Dicyanostilbene* has been prepared together with the *trans*-isomer from  $\alpha$ -cyanobenzyl thiocyanate and the configuration of the *cis*-isomer proved by chemical and spectroscopic methods.

$\alpha\beta$ -DICYANOSTILBENE, m. p. 161°, has been shown by its acid-induced cyclisation, its light absorption,<sup>1</sup> and X-ray crystal structure,<sup>2</sup> to be the *trans*-isomer. The literature contains two claims to the preparation of the *cis*-isomer. Prolonged ultraviolet irradiation of the *trans*-isomer gave an isomer, m. p. 199—204°,\* at first thought to be the *cis*-isomer,<sup>3</sup> but since shown to be *trans*-9,10-dicyano-9,10-dihydrophenanthrene.<sup>4</sup> Kretov and Pantschenko<sup>5</sup> claimed to have prepared an isomer of  $\alpha\beta$ -dicyanostilbene by hydrolysis of di-( $\alpha$ -cyanobenzyl) sulphide, or  $\alpha$ -cyanobenzyl thiocyanate with alcoholic potassium hydroxide, with m. p. 240 and 243°, respectively. On further alkaline hydrolysis the isomer yielded diphenylmaleic anhydride (I). We have attempted to repeat Kretov and Pantschenko's work, but could only isolate 2-imino-5-oxo-3,4-diphenyl- $\Delta^3$ -pyrroline (II), m. p. 250—252° (decomp.). This compound had previously been prepared by Banfield,<sup>6</sup> by hydrolysis of 5-guanidino-2-imino-3,4-diphenyl-2*H*-pyrrole (III). The structure is supported by the presence of two NH, a C=O, and a C=N band in the i.r. spectrum, and by hydrolysis under mild acidic conditions to diphenylmaleimide (IV).



*cis- $\alpha\beta$ -Dicyanostilbene*, m. p. 134°, has now been obtained by treatment of an ethanolic solution of  $\alpha$ -cyanobenzyl thiocyanate with cold aqueous ammonia, and separation of the

\* Varies with rate of heating.

<sup>1</sup> Part I, Coe, Gale, Linstead, and Timmons, *J.*, 1957, 123.

<sup>2</sup> (a) Timmons and Wallwork, *Chem. and Ind.*, 1955, 62; (b) Wallwork, *Acta Cryst.*, 1961, **14**, 375.

<sup>3</sup> Coe, Garnish, Gale, and Timmons, *Chem. and Ind.*, 1957, 665.

<sup>4</sup> (a) Sargent and Timmons, *J. Amer. Chem. Soc.*, 1963, **85**, 2186; (b) Sargent and Timmons, unpublished results.

<sup>5</sup> Kretov and Pantschenko, *J. Russ. Phys., Chem. Soc.*, 1929, **61**, 1975.

<sup>6</sup> Banfield, *J.*, 1960, 2108.

mixture of *cis*- and *trans*-isomers produced. Previously,<sup>1</sup> the *cis*-isomer had not been isolated from this reaction.

Similarities are apparent between the n.m.r. spectra of the geometrical isomers of stilbene<sup>7</sup> and those of  $\alpha\beta$ -dicyanostilbene. *cis*-Stilbene, in deuteriochloroform solution, shows a singlet at  $\tau$  2.82 due to the aromatic protons; similarly *cis*- $\alpha\beta$ -dicyanostilbene in dimethyl sulphoxide solution exhibits a singlet at  $\tau$  2.40. *trans*-Stilbene, in deuteriochloroform solution has a highly split signal at  $\tau$  2.38 to 2.80, due to the aromatic protons. The same complex signal for the aromatic protons of *trans*- $\alpha\beta$ -dicyanostilbene appears between  $\tau$  1.95 and 2.39 in dimethyl sulphoxide. This evidence is indicative of a *cis*-configuration for the isomer of  $\alpha\beta$ -dicyanostilbene, m. p. 134°.

For *trans*-tetrasubstituted ethylenes the C=C vibration in the i.r. spectrum, is expected, due to symmetry, to be unobserved or of very low intensity. Felton and Orr<sup>8</sup> have claimed to observe a C=C vibration at 1619 cm.<sup>-1</sup> ( $\epsilon^a$  10) in *trans*- $\alpha\beta$ -dicyanostilbene. We have been unable to observe this band even at high concentration, but have observed a band at 1635 cm.<sup>-1</sup> ( $\epsilon^a$  2.3) probably due to the C=C vibration. Two bands are present in the aromatic C=C vibration region at 1599 cm.<sup>-1</sup> ( $\epsilon^a$  13.5) and 1581 cm.<sup>-1</sup> ( $\epsilon^a$  8.5). The latter band indicates that the phenyl group is conjugated with the double bond.<sup>9</sup> For *cis*- $\alpha\beta$ -dicyanostilbene a band is observed at 1616 cm.<sup>-1</sup> ( $\epsilon^a$  6.6) which is assigned to the C=C vibration. The aromatic C=C vibrations occur at 1600 cm.<sup>-1</sup> ( $\epsilon^a$  17.1) and 1589 cm.<sup>-1</sup> ( $\epsilon^a$  17.7).

The u.v. spectra of the isomeric dicyanostilbenes and some related compounds are shown in the Table. Alkyl substitution of the stilbene double-bond causes a shift of the *K*-bands of both *cis*- and *trans*-isomers to progressively shorter wavelength, accompanied by a similar decrease in extinction coefficient, as the size and number of the alkyl groups is increased. The *cis*- $\alpha\beta$ -dimethyl- and *cis*- $\alpha\beta$ -diethyl-stilbenes absorb at longer wavelength than the corresponding *trans*-isomers, although the intensities are lower than for the *trans*-isomers.

Electronic spectra of stilbenes.

Substituents	<i>trans</i>		<i>cis</i>	
	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon_{\max.}$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon_{\max.}$
None <sup>a</sup> .....	228, 295 *	16,400, 29,000	224, 280	24,400, 10,500
$\alpha$ -Me <sup>b</sup> .....	272	21,000	267	9300
$\alpha\beta$ -Me <sub>2</sub> <sup>b</sup> .....	243	12,300	252	8800
$\alpha\beta$ -Et <sub>2</sub> <sup>b</sup> .....	237	11,000	244	7700
$\alpha$ -CN <sup>cd</sup> .....	229, 311	15,000, 23,000	224, 295	23,000, 16,600
$\alpha\beta$ -(CN) <sub>2</sub> <sup>c</sup> .....	236, 324	12,000, 19,000	227, 273	12,900, 6800
			320	11,200

<sup>a</sup> Beale and Roe, *J.*, 1953, 2755. <sup>b</sup> Suzuki, *Bull. Chem. Soc. Japan.*, 1952, **25**, 145. <sup>c</sup> Ref. 1.

<sup>d</sup> Coddington and Mosettig, *J. Org. Chem.*, 1957, **17**, 1023.

\* Main band; there is also vibrational fine structure.

This suggests that the *cis*-isomers have configurations in which the angle of twist of the phenyl groups about the plane of the double bond is less than that of the *trans*-isomers, but that the chromophores of the *trans*-isomers are more extended, and hence the *K*-band is of greater intensity. Nitrile substitution, and hence conjugation of the double bond, causes a bathochromic shift in both *cis*- and *trans*-series. *cis*- $\alpha\beta$ -Dicyanostilbene appears to be less planar than the *trans*-isomer since its *K*-band is at shorter wavelength than that of the *trans*-isomer. The light absorption of *cis*- $\alpha\beta$ -dicyanostilbene is probably more similar to stilbene than to the  $\alpha\beta$ -disubstituted alkyl stilbenes because the nitrile group is linear and occupies less space than the ethyl and methyl groups.

<sup>7</sup> Bhacca, Johnson, and Shooley, "N.M.R. Spectra Catalog," Varian Associates, Palo Alto, 1962.

<sup>8</sup> Felton and Orr, *J.*, 1955, 2170.

<sup>9</sup> Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 72.

Pfeiffer *et al.*<sup>10</sup> reported that nuclear-substituted *trans*- $\alpha$ -cyanostilbenes on treatment with concentrated sulphuric acid gave substituted 2-phenylinden-1-ones, and that the *cis*-isomers were not cyclised. *trans*- $\alpha\beta$ -Dicyanostilbene on treatment with concentrated sulphuric acid gives a mixture of 3-carbamoyl-2-phenylindenone and 3-cyano-2-phenylindenone.<sup>1</sup> *cis*- $\alpha\beta$ -Dicyanostilbene under identical conditions has now been shown to give diphenylmaleic anhydride (I), as expected. This reaction demonstrates the *cis*-arrangement of the phenyl groups about the double bond.

Alkaline hydrolysis<sup>11-13</sup> of *trans*- $\alpha\beta$ -dicyanostilbene is accompanied by inversion to yield diphenylmaleimide (IV) and diphenylmaleic anhydride (I). The *cis*-isomer also gives diphenylmaleimide. It has been shown recently<sup>4,14,15</sup> that ultraviolet irradiation of stilbenes in the presence of hydrogen acceptors, usually oxygen, affords phenanthrenes by dehydrocyclisation. *trans*- $\alpha\beta$ -Dicyanostilbene in the presence of oxygen gives 9,10-dicyanophenanthrene.<sup>3,4</sup> Irradiation of *cis*- $\alpha\beta$ -dicyanostilbene also produces 9,10-dicyanophenanthrene.

*trans*- $\alpha\beta$ -Dicyanostilbene on fusion with various salts or metals yields octaphenyltetraazaporphins.<sup>16</sup> The *cis*-isomer reacts similarly.

### EXPERIMENTAL

Melting points were determined on a Kofler block and are corrected. Ultraviolet spectra refer to ethanolic solutions and were determined on a Unicam S.P. 700 spectrophotometer. Infrared spectra were determined on a Unicam S.P. 100 spectrophotometer with a prism-grating double monochromator and refer to chloroform solutions unless otherwise stated. The intensities quoted ( $\epsilon^a$ ) are the apparent values, as observed with a spectral slit width of about 2 cm.<sup>-1</sup>. Nuclear magnetic resonance spectra were determined with an A.E.I. RS2 spectrometer at 60 Mc./sec., with tetramethylsilane as internal standard and refer to dimethyl sulphoxide solutions.

*2-Imino-5-oxo-3,4-diphenyl- $\Delta^3$ -pyrroline* (II) (with DR. D. G. COE).—(a)  $\alpha$ -Cyanobenzyl thiocyanate<sup>1</sup> (57.2 g.) was added to a solution of potassium hydroxide (57.2 g.) in ethanol (300 ml.), and the solution heated to boiling and then poured immediately into water (3 l.). The green precipitate was filtered off and washed with ice-cold ethanol (200 ml.), which removed most of the green colour. Crystallisation from chloroform (charcoal) gave the oxo-imine as pale yellow needles (20.4 g.; 45%), m. p. 250—252° (decomp.) [lit.,<sup>6</sup> 244—249° (decomp.)] (Found: C, 77.3; H, 5.0; N, 11.1. Calc. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O: C, 77.4; H, 4.9; N, 11.3%);  $\lambda_{\max}$ . 224.5, 238.5, 251, 271, and 330 m $\mu$  ( $\epsilon$  14,300, 13,200, 12,400, 14,100, and 4600, respectively);  $\lambda_{\max}$ . in 0.1N-ethanolic potassium hydroxide, 210, 228.5, and 287 m $\mu$  ( $\epsilon$  21,100, 18,700, and 17,700, respectively);  $\nu_{\max}$ . 3446 ( $\epsilon^a$  105, imide-NH), 3313 ( $\epsilon^a$  103, imine-NH), 1742 ( $\epsilon^a$  641, C=O), and 1663 ( $\epsilon^a$  754, C=N) cm.<sup>-1</sup>;  $\tau$  2.45 (singlet, aromatic protons). (b) Di-( $\alpha$ -cyanobenzyl) sulphide<sup>5</sup> (1.6 g.) was added to a solution of potassium hydroxide (0.7 g.) in ethanol (10 ml.), heated to boiling, and then poured at once into water (50 ml.). The greenish solid was filtered off, and washed with much water and a small quantity of ethanol. The oxo-imine (1.2 g.; 80%) crystallised from benzene and then from ethanol-chloroform (1 : 1 v/v) as pale yellow needles, m. p. 250—252° (decomp.) undepressed on mixture with that prepared from  $\alpha$ -cyanobenzyl thiocyanate.

*Diphenylmaleimide* (IV).—(a) The oxo-imine (3.1 g.) was dissolved in ethanol (120 ml.), hydrochloric acid (0.1N; 300 ml.) was added, and the solution was warmed on the water-bath for 0.5 hr. On cooling, yellow needles of the imide (2.6 g.; 86%) crystallised from the solution. The product, when crystallised from ethanol, had m. p. 219.5° undepressed on mixture with an authentic sample;  $\lambda_{\max}$ . 224, 263, 307, and 353 m $\mu$  ( $\epsilon$  15,700, 8600, 3400, and 5100, respectively);

<sup>10</sup> Pfeiffer, Behr, Kübler, and Rüping, *J. prakt. Chem.*, 1929, **121**, 85.

<sup>11</sup> Reimer, *Ber.*, 1880, **13**, 742; 1881, **14**, 1797.

<sup>12</sup> Korchak and Lisseenko, *J. Gen. Chem. (U.S.S.R.)*, 1939, **9**, 1329.

<sup>13</sup> Rügheimer, *Ber.*, 1882, **15**, 1625.

<sup>14</sup> Hügelschofer, Kalvoda, and Schaffner, *Helv. Chim. Acta*, 1960, **43**, 1322.

<sup>15</sup> Moore, Morgan, and Stermitz, *J. Amer. Chem. Soc.*, 1963, **85**, 830.

<sup>16</sup> Cook and Linstead, *J.*, 1937, 929.

$\lambda_{\text{inf}}$ , 249.5 and 319  $\mu$  ( $\epsilon$  11,900 and 3600, respectively);  $\nu_{\text{max}}$  3439 ( $\epsilon^a$  102, free NH), 3200 ( $\epsilon^a$  49, H-bonded NH), 1782 and 1734 ( $\epsilon^a$  179 and 1660 respectively, C=O)  $\text{cm}^{-1}$ ;  $\tau$  2.45 (singlet, aromatic protons) and  $-1.61$  (broad singlet, NH proton).

(b) *cis- $\alpha\beta$ -Dicyanostilbene* (0.642 g.) was heated under reflux with methanol (75 ml.) containing sodium hydroxide (2 g.) for 4 days and then poured into water (200 ml.). The solution was acidified with concentrated hydrochloric acid and extracted with ether ( $3 \times 100$  ml.). The ether extract was dried ( $\text{MgSO}_4$ ); removal of the solvent gave crude diphenylmaleimide (0.460 g.). After two recrystallisations from ethanol the imide had m. p.  $219^\circ$ , undepressed on mixture with an authentic sample, and the i.r. spectrum was superposable with that of an authentic sample.

*Diphenylmaleic Anhydride* (I).—*cis- $\alpha\beta$ -Dicyanostilbene* (0.245 g.) was dissolved in cold concentrated sulphuric acid (20 ml.), set aside for 20 hr., and then heated for 0.5 hr. on the water-bath. The solution was poured over ice-cubes, and the product filtered off, washed with water, and dried. On crystallisation from acetone, diphenylmaleic anhydride (0.196 g.), m. p.  $155-156^\circ$  undepressed on mixture with an authentic sample, was obtained as pale yellow needles;  $\lambda_{\text{max}}$  252.5, 275, and 347  $\mu$  ( $\epsilon$  7200, 5600, and 6100, respectively);  $\nu_{\text{max}}$  1840 and 1770  $\text{cm}^{-1}$  ( $\epsilon^a$  164 and 1740, respectively; anhydride C=O);  $\tau$  2.35 (singlet; aromatic protons).

*cis- and trans- $\alpha\beta$ -Dicyanostilbene*.—To a solution of  $\alpha$ -cyanobenzyl thiocyanate (115 g.) in ethanol (700 ml.) was added aqueous ammonia (300 ml.;  $d$  0.88), and the mixture cooled to room temperature and stirred mechanically for 0.5 hr. The precipitate was filtered off, washed with a small amount of ice-cold ethanol, and crystallised from benzene, giving needles of *trans- $\alpha\beta$ -dicyanostilbene* (43.2 g.; 52%), m. p.  $161-162^\circ$ ;  $\nu_{\text{max}}$  3087 ( $\epsilon^a$  11.9), 2220 ( $\epsilon^a$  37, C $\equiv$ N), 1635 ( $\epsilon^a$  2.3, C=C), 1599 ( $\epsilon^a$  13.5, C=C), 1581 ( $\epsilon^a$  8.5, C=C), 1497 ( $\epsilon^a$  23.2), 1471 ( $\epsilon^a$  6.8), 1341 ( $\epsilon^a$  5.9), 1109 ( $\epsilon^a$  7.8), 1021 ( $\epsilon^a$  20.1), and 1002 ( $\epsilon^a$  15.7)  $\text{cm}^{-1}$ ;  $\nu_{\text{max}}$  (KBr) 1597, 1581, 1497, 1449, 1341, 1322, 1290, 1252, 1185, 1160, 1108, 1080, 1037, 1023, 1005, 959, 918, and 757  $\text{cm}^{-1}$ ;  $\tau$  1.95—2.39 (aromatic protons). *cis- $\alpha\beta$ -Dicyanostilbene* (3.67 g.; 4.6%), m. p.  $134^\circ$ , was obtained as prisms by allowing the mother-liquors to crystallise in the dark [Found: C, 83.2; H, 4.3; N, 12.4%;  $M$  (Rast), 221.  $\text{C}_{16}\text{H}_{10}\text{N}_2$  requires C, 83.5; H, 4.4; N, 12.2%;  $M$ , 230]; Electronic spectrum, see Table;  $\nu_{\text{max}}$  3069 ( $\epsilon^a$  25.1), 2220 ( $\epsilon^a$  52, C $\equiv$ N), 1616 ( $\epsilon^a$  6.6, C=C), 1600 ( $\epsilon^a$  17.1, C=C), 1589 ( $\epsilon^a$  17.7, C=C), 1562 ( $\epsilon^a$  14.5), 1494 ( $\epsilon^a$  32), 1451 ( $\epsilon^a$  77), 1324 ( $\epsilon^a$  23.4), 1305 ( $\epsilon^a$  61), 1281 ( $\epsilon^a$  36), 1114 ( $\epsilon^a$  6.6), 1074 ( $\epsilon^a$  16.7), 1032 ( $\epsilon^a$  9.5), 1011 ( $\epsilon^a$  28.3), 961 ( $\epsilon^a$  17.8), and 923 ( $\epsilon^a$  16.6)  $\text{cm}^{-1}$ ;  $\nu_{\text{max}}$  (KBr) 1599, 1589, 1563, 1493, 1449, 1389, 1324, 1305, 1282, 1235, 1186, 1163, 1111, 1074, 1030, 1003, 958, 921, 864, 844, and 760  $\text{cm}^{-1}$ ;  $\tau$  2.40 (singlet, aromatic protons). No other signals were present when the n.m.r. spectrum was recorded for a chloroform solution.

*Copper Octaphenyltetra-azaporphin Chloride*.—*cis- $\alpha\beta$ -Dicyanostilbene* (2.0 g.) was fused with cuprous chloride in the manner described by Cook and Linstead,<sup>16</sup> and gave the pigment (1.2 g.) as a black crystalline powder from chloroform; it had  $\lambda_{\text{max}}$  in  $\text{CHCl}_3$  585, 641, and 709  $\mu$  ( $\epsilon$  47,500, 49,500, and 38,600, respectively).

*Photolysis of cis- $\alpha\beta$ -Dicyanostilbene*.—*cis- $\alpha\beta$ -Dicyanostilbene* ( $5.05 \times 10^{-4}$  M) in ethanol in a 0.1-cm. silica absorption cell was photolysed 1 cm. in front of a Hanovia 400 w medium-pressure mercury lamp surrounded by a Pyrex water-cooling jacket. After 5 min. the u.v. spectrum showed peaks at 320, 333, 360, and 380  $\mu$ , characteristic of 9,10-dicyanophenanthrene.<sup>3</sup>

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